



## PRODUCING METHOD AND PRODUCING APPARATUS OF NUCLEAR SPIN POLARIZED XENON GAS

### BACKGROUND

This invention relates to a method and apparatus for producing  
5 nuclear spin polarized xenon gas, and more specifically, relates to  
continuously producing highly concentrated nuclear spin polarized  
xenon gas capable of producing a polarized nuclear spin useful for  
NMR+MRI apparatus.

It has been recently reported that when xenon gas with a nuclear  
10 spin polarized (nuclear spin polarized xenon gas) is applied to  
NMR+MRI method, detection sensitivity is enhanced rapidly.

The term 'polarized' as used herein means that distribution of  
the spin number occupying energy order of nuclear spins of an atomic  
nucleus corresponding to the orientation state with respect to the metal  
15 static magnetic field is extremely one-sided.

To obtain a rare gas having the polarized state circularly  
polarized excitation light is irradiated on gas having rare gas including  
a single atomic molecule having a nuclear spin of spin quantum number  
1 12 such as xenon-129 ( $^{129}\text{Xe}$ ), helium-3 ( $^3\text{He}$ ) or the like mixed with  
20 alkali metal vapor such as rubidium, cesium or the like. An electron in

the base state order of rubidium or the like is excited by light absorption in the base state order and returned to the base state order after passage of the base state order, at which time it is transited with high probability to one order of electron orders out of the base state orders whose degeneracy is released magnetically by a magnetic field. The magnetic field is applied from outside to prepare the state that an electronic spin polarization degree of a rubidium molecule or the like is high, and the rubidium or the like in the high polarization state collides with rare gas such as xenon, at which channel the high polarization state of rubidium or the like moves to a nuclear spin system of rare gas such as xenon. This channel is generally called optical pumping.

In the conventional polarized rare gas producing apparatus, a mixed gas of rare gas and alkali metal vapor is confined into an optical reaction vessel, to which irradiation of excited light and application of magnetic field are carried out. For example, there is a producing apparatus, for the purpose of using polarized helium-3 of high density as a neutral polarizer, in which a mixed gas of helium-3 gas and nitrogen gas and alkali metal are confined into a cylindrical glass ample (for example, see M.E. Wagshul and T.E. Chu PP, Phy, Rev. A40, 4447 (1989)).

On the other hand, there is an apparatus in which for example, 1% of xenon is mixed with buffer gas of helium of 10 atmospheric

pressure or so, introduced into a cylindrical glass vessel, irradiated, polarized, and guided into Dewar cooled by liquid nitrogen from a gas outlet of the vessel. Polarized xenon is formed into a solid, which is separated. The remaining helium gas is discharged from a vent line  
5 (For example, see B. Driehuys, G.D. Cates, E. Miron, K. Sauer, D.K. Walter and W. Happer, Appl. Phys, Lett. 69, 1668(1996).

In any of those apparatuses as noted above, operation for enhancing the polarization rate is carried out by receiving a laser beam in the state that rare gas or the like is stayed in an optical reaction  
10 vessel. With the polarization rate enhanced, and after the temperature cooled to a room temperature, the gas may be used as a neutral polarizer as it is, or polarized as xenon 129 once solid-separated within Dewar is heated again into gas. Then it is transferred to a separate vessel for use in measurement of NMR or the like.

15 However, in the above-mentioned conventional method, for facilitating polarization, xenon is diluted, for example, to helium 2% xenon concentration or so. Polarized gas containing produced xenon then is frozen with liquid nitrogen, which is heated to remove only the xenon to produce high concentration xenon gas, thus posing a problem  
20 that work efficiency is extremely poor. In addition, in the conventional apparatus in which gas or the like is stayed and polarized, since polarized gas cannot be generated continuously, polarized gas is taken

out into a separate vessel every time and carried to NMR apparatus, thus taking time, and posing a problem that the polarization rate reduces during such a period of time as described.

This invention has been accomplished in view of the foregoing,  
5 and has its object to provide producing method and producing apparatus capable of obtaining polarized xenon gas of high concentration without being frozen, and capable of generating polarized xenon gas continuously.

It is a further object of this invention to provide producing  
10 method and producing apparatus of a glass cell in which metal rubidium and xenon gas used for the above-described producing method and producing apparatus are solidified and sealed under the absence of oxygen.

## SUMMARY OF THE INVENTION

15 A glass cell having solid rubidium and solid xenon filled in the pressure reducing state of being absent in oxygen is heated to be gas xenon and gas-liquid mixed rubidium, to which a magnetic field is applied to irradiate a laser beam. It is noted that being absent in oxygen termed herein is meant not to oxidize solid rubidium, and the

presence of a fine amount of oxygen to a degree that even if solid rubidium is oxidized, reaction is not affected, is allowed.

When the thus produced nuclear spin polarized xenon gas is taken out, pressure naturally lowers and air flows backward into the glass cell. Therefore, xenon polarized gas is taken out while  
5 introducing xenon gas so as to maintain fixed pressure. Further, by doing so, polarized xenon gas can be produced continuously.

Preferably, it is constituted so that in replacing a xenon gas supply device, the xenon gas supply device side is made to be a primary side through a first air operate valve, and the xenon gas  
10 introducing side of the glass cell is made to be a secondary side, and vacuuming of the primary side piping and pressurization-leaving by nitrogen gas are repeated automatically more than three times.

Preferably, in replacing the glass cell, vacuuming of piping from the primary side piping, the secondary side pipe and the primary side pipe to a valve on the polarized xenon gas take-out side  
15 communicated through a second air operate valve and pressurization-leaving by nitrogen gas are repeated automatically more than three times.

To produce a glass cell according to the present invention a chamber houses a glass vessel filled with rubidium. The chamber and  
20

said glass cell are connected so that they are in communication by piping. The piping is exhausted by a vacuum generator, after which the glass vessel filled with rubidium is broken, and the metal rubidium, piping and glass cell heated. As a result rubidium gas is made present  
5 within the piping and glass cell. Then the glass cell is cooled, metal rubidium is precipitated as a solid into the cooled portion, xenon gas is introduced into the glass cell and closed, and the glass cell is cooled to solidify xenon within the glass cell.

An apparatus for carrying out the present invention, includes  
10 means for heating a glass cell having solid rubidium and solid xenon filled in the pressure reducing state, in which oxygen is absent, to achieve gas xenon and gas-liquid mixed rubidium, and means for applying a magnetic field to the glass cell to irradiate a laser beam.

Further, preferably, there comprises means for introducing  
15 xenon gas while taking out the produced nuclear spin polarized xenon gas, and pressure regulating means for controlling said operation so that pressure may not drop.

Piping from a xenon gas supply to a first air operate valve serves as primary side piping. Piping from auch first air operate valve  
20 to a valve for introducing xenon gas into the glass cell serves as secondary side piping. Provided on the primary side are branched

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5 pipings and pressure regulating means. The branched pipings are connected to said primary side piping through a second air operate valve. One of said branched pipings reaches a vacuum generator and another reaches a valve on the xenon gas taking-out side of said glass cell. The pressure regulating means regulates pressure introduced into the glass cell.

10 An apparatus for producing a glass cell according to the present invention includes piping connected so that a chamber housing rubidium filled into a glass vessel and the glass cell are connected. Also included are means for vacuuming the piping, means for breaking glass having rubidium filled in, means for heating the metal rubidium, piping and glass cell, and means for cooling the glass cell and precipitating metal rubidium on the cooled portion.

15 In summary, the gist of the present invention lies in that xenon is filled into the glass cell having metal rubidium adhered thereto heated to irradiate a laser beam thereby obtaining polarized xenon gas of high concentration without being frozen.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 is a schematic sectional view showing a producing apparatus of a glass cell having rubidium and xenon filled therein according to the present invention.

FIG 2 is a sectional view showing the state that rubidium and xenon are filled in, and thereafter a glass cell is closed and sealed.

FIG 3 is a structural view showing one embodiment of the producing apparatus according to the present invention.

#### DETAILED DESCRIPTION

In the following, the embodying form of the present invention will be described with reference to the drawings.

FIG 1 shows a glass cell having rubidium and xenon filled in, in which a vacuum pump 5 and a xenon gas supply line 6 are connected to piping 4 connecting a metal rubidium 1 enveloped with glass housing chamber 2 and a glass cell 3. When rubidium comes in contact with air, it is oxidized and changed into oxide of rubidium, and therefore in case of purchasing it from makers, it is filled in glass as described above. It is noted that in this state, a valve Vxe, a valve V1 and a valve V2 are closed.



If a valve  $V_p$  is opened, in the state that the valve  $V_{xe}$  is closed, to exhaust by the vacuum pump 5, air in the piping 4 and the glass cell 3 is exhausted. When, in this state, glass in which rubidium is filled is broken, metal rubidium will be present in vacuum, thus not being oxidized. A magnet 21 enveloped with glass is also filled in the metal rubidium 1 housing chamber 2. The magnet 21 is moved by a magnet 23 from outside into contact with metal rubidium 1 to break the glass.

Next, the metal rubidium 1, glass cell 3 and piping 4 are wholly heated by a heating device 25. It is suggested that a heating temperature is not less than a melting point (about  $40^{\circ}\text{C}$ ) of rubidium, and is a temperature that rubidium assumes a gas-liquid mixed state in which liquid and gas of a vapor pressure portion at that temperature are present with high concentration. More specifically, preferably,  $130 - 180^{\circ}\text{C}$ , particularly preferably, near  $150^{\circ}\text{C}$ .

Then, when only a part of glass cell is cooled, rubidium in the gas state is solidified on only the cooled part and separated as shown in FIG 3.

Then, when the vacuum pump 5 side valve  $V_p$  is closed and  $V_{xe}$  is opened, gaseous xenon is introduced into the glass cell 3. Next, when  $V_{xe}$  is closed, and the whole glass cell 3 is cooled with liquid

nitrogen, xenon is turned to solid. Originally, since xenon is introduced into solid rubidium confined in vacuum, if xenon is solidified, the glass cell assumes a pressure reducing state (vapor pressure at a liquid nitrogen temperature).

5           In this state, if a portion 8 depicted in FIG. 2 is heated and molten by operation of a burner, the glass cell 3 having solid rubidium and solid xenon filled in is obtained. The glass cell then may be used in a system as shown in FIG. 3 to produce the polarized xenon gas.

10           Referring to FIG. 3, when a heating device 33 heats the glass cell 3 to elevate the temperature of the glass cell 3, preferably, to 50 -180°C, particularly preferably, near 120°C, the glass cell contents will internally become xenon gas and gas-liquid mixed rubidium. In this state, if a magnetic field is applied by a magnetic  
15           source 35 to irradiate laser, xenon gas will be nuclear spin polarized xenon gas in scores of minutes.

          Referring to FIG 3, when the valves V2 and V3 are opened, polarized xenon gas is collected by a polarized xenon gas collecting cylinder 9. At the same time, the valve V1 may be opened to introduce  
20           xenon gas while regulating pressure by an auto pressure regulator (APC) 10, so that pressure may not drop. When polarized xenon gas in the glass

cell 3 is taken out, pressure lowers and the air back flows, because of which the pressure-regulate xenon gas is introduced as described above. It is noted that in this state, air operate valves AV6, AV 1 and AV3, and valves V1. V2 and V3 in FIG 3 are opened.

5           Then, the valves V1 and V2 are closed, the whole glass cell 3 is cooled with liquid nitrogen, and after xenon is solidified. The glass cell 3 then is heated to produce polarized xenon gas by the same operation as mentioned above. In this manner, it can be produced repeatedly continuously till rubidium as a catalyst is gone.

10           As also shown in FIG 3, xenon gas from a xenon cylinder 11 may be introduced from the valve V1 of the glass cell 3 passing through an air operate valve (AV 1), an auto pressure regulator (APC) 10 and a first air operate valve (AV3). In this embodiment, since pressure for taking out polarized xenon gas is 1.5 atmospheric pressure or so, pressure of xenon gas is regulated to the same 1.5  
15           atmospheric pressure or so by APC 10. In FIG. 3, valves V1 - V4 are constituted by glass valves because polarized gas comes in contact, and because if glass is not employed, polarized xenon gas returns to xenon gas. Accordingly, other portions within piping with which  
20           polarized xenon gas contacts are also glass (pyrex).

Nitrogen gas and xenon gas are dropped down to pressure of 1.5 atmospheric pressure or so by pressure reducing valves (REG 2 and REG 1), respectively.

In the above-described reaction, it is necessary that air may not enter at all the glass cell. Because even if a small amount of air is mixed, the rubidium catalyst is oxidized, resulting in not exhibiting the catalyst function.

Air is mixed in at the time of replacing a cylinder and at the time of replacing a glass cell, in which case, air is prevented from mixing into the glass cell in the following manner.

In case of replacing a xenon cylinder, air is mixed into piping between an original valve 13 of the cylinder, an air operate valve (AV 1) and an air operate valve (AV6). For removing the air, a vacuum pump (P) 15 is turned on, an air operate valve (AV 1) and air operate valve (AV2) and a second operate valve (AV4) are opened to vacuum piping on the primary side, and the state is left as it is for a fixed time while detecting a pressure reducing degree by a pressure transmitter ((PT1). Through the first air operate valve (AV3), the xenon gas supply device side is made to be a primary side, and the xenon gas introducing side of the glass cell is made to be a secondary side. Piping between the introducing valve at the glass cell 3 and the first air operate valve

(AV3) is referred to herein as secondary side piping 39. Piping between the xenon gas supply device 11 and the first air operate valve is referred to herein as primary side piping 37.

Then, the second air operate valve (AV4) is closed to pressurize the interior of piping on the primary side with nitrogen gas. The pressure on the primary side is left for fixed time preset while detecting it by the pressure transmitter (PT 1). Then, the step is again repeated for vacuuming again the interior of piping on the primary side and pressurizing the interior of piping on the primary side with nitrogen gas to leave it. Preferably, it is possible to prevent oxygen from mixing into the glass cell by repeating the step more time 10 times.

When the glass cell is replaced, air is mixed into the piping between piping to the manual valve V1 at a glass cell inlet on the secondary side in communication with piping on the primary side through the first air operate valve (AV3), the manual valve V2 for taking out polarized gas, the valve V3 or controlling the flow into the collecting portion, and the valve V4 for controlling the communication with the vacuum pipe.

The valve V4 and the second air operate valve (AV4) (controlling communication between piping on the primary side and the vacuum pump) are opened to vacuum the interior of piping of the

air mixing portion. Then, the first air operate valve from the both  
cylinder 11,12 (AV3) connecting pipings on the primary side and  
secondary side, and the valve to the first air operate valve (AV3) are  
opened to pressurize piping on the primary side and piping on the  
5 secondary side with nitrogen gas, and all the valves are closed for  
pressurization-leaving. Then, the step is repeated for opening the first  
air operate valve and the second air operate valve, vacuuming similar  
to that mentioned above, and pressurization-leaving. Preferably, it is  
possible to prevent oxygen from mixing into the glass cell by  
10 repeating the step more than 10 times. Since the pressure transmitter  
(PT2) is disposed on piping on the secondary side, vacuuming and  
pressurization-leaving are performed for fixed time pre-set while  
sensing pressure. The air operate valve (AV5) in FIG 3 is a valve for  
releasing gas when the interior of the primary piping is in the  
15 pressurizing state, which is however not used in the above-described  
operation.

In FIG. 3, while nitrogen and xenon gas are supplied from  
the cylinder, well known other gas supply devices will suffice.

According to the present invention, reaction is done with  
20 high concentration such as xenon gas 80 - 100% (remainder,  
nitrogen gas) to thereby obtain polarized xenon gas, thus obtaining

polarized xenon gas of high concentration without carrying out treatment such as solidifying after being polarized.

5 Further, vacuuming the interior of piping and pressurization-leaving can be carried out many times to prevent air from flowing into the glass cell.

As described above, according to the present invention, since xenon gas of high concentration can be used to produce polarized xenon gas of high concentration, trouble of concentrating by freezing after production as in prior art can be eliminated.

10 Further, xenon gas as raw material is regulated in pressure and introduced while taking out polarized xenon gas, whereby back-flow of air is prevented, and polarized xenon gas can be produced continuously.

15 Furthermore, vacuuming the interior of piping and pressurization-leaving are carried out repeatedly to thereby sufficiently enable purging the interior of piping, and so, it is possible to prevent mixing of air in the reaction glass cell, and to extend the life of the rubidium catalyst.

20 Accordingly, it is expected to utilize the invention as producing method and producing apparatus of producing polarized

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nuclear spin polarized xenon gas useful for NMR•MRI apparatus  
with high concentration and continuously.